Synopsis

Ph.D. in Chemistry

Investigation of Biomass Derived Functional Carbon Electrodes from leaves of *Spathodea campanulata* and *Tecoma capensis* for Supercapacitor applications

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Submitted to

Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore - 641 043

April - 2024

Introduction

Energy storage devices play a pivotal role in the storage and release of electric energy as require, serving as a critical solution in the fight against global warming. As society increasingly relies on renewable energy generation and highly efficient automobile systems, the significance of energy storage device technology continues to grow.

Supercapacitors are classified into two main types based on their charge storage mechanisms: electric double-layer capacitors (EDLCs) and pseudo capacitors. EDLCs store charge through the physical adsorption of ions onto the surface of electrodes, while pseudo capacitors involve fast, reversible redox reactions at the electrode/electrolyte interface.

Biomass, typically associated with plant materials, encompasses a broad range of organic molecules, including carbon, hydrogen, oxygen, and nitrogen. In recent years, there has been growing interest in the development of carbon materials derived from biomass precursors for various applications. These carbon materials exhibit remarkable properties and can be easily obtained from biomass-based industries and environmental sources.

Carbon materials derived from biomass have shown remarkable performance in a wide range of applications, including supercapacitor electrodes, dye-sensitized solar cells, catalysts, and energy storage devices such as sodium-ion batteries and potassium-ion batteries. Additionally, they have been utilized in applications such as microwave absorption, dye removal, metal ion removal, and pesticide/herbicide removal.

A recent trend in the field of carbon supercapacitor electrodes involves the utilization of biomass waste materials to produce activated carbons, featuring electrodes derived from biomass sources such as European deciduous trees, poplar catkins, celery, and various agricultural residues, hold great promise for sustainable energy storage solutions. The utilization of biomass waste materials not only addresses environmental concerns but also contributes to the development of cost-effective energy storage technologies.

Literature Review

A systematic review was carried out by collecting research papers related to Supercapacitor application studies by various techniques, theoretical studies, using various article data bases such as Scifinder and Scopus over five decades (1970-2020). Plants names and families were authenticated by Botanical Survey of India. Up to date knowledge of all current issues relating to supercapacitors were studied to gain an insight into the framing of methodology.

Research Gap

Literature survey reflects that there has been no investigation utilizing *Spathodea campanulata* and *Tecoma capensis* as precursors for the synthesis of carbon materials specially for supercapacitors applications. This finding highlights an important research gap in the production of carbon materials suitable for supercapacitor electrodes. Given the abundance of these plant species, exploration of their potential as precursors for carbon materials could lead to the development of novel and sustainable approaches for energy storage, contributing to the advancement of supercapacitor technology and addressing the growing demand for efficient and eco-friendly energy storage solutions.

From the literature survey, the highest capacitance obtained from biomass-derived carbon supercapacitors has been reported to be around 400-500 F/g (farads per gram). However, its essential to note that it may vary depending on the specific biomass material used, the fabrication method, and the testing conditions (Yang Liu *et al*.,2018). Researchers are continually exploring new biomass sources and optimizing fabrication processes to enhance the capacitance further. In this quest the present work is focused on attaining much higher capacitance than already reported.

The application of *Spathodea campanulata* and *Tecoma capensis* based carbon electrode for energy storage applications is lacking highlighting the existence of the research gap.

Objectives

The research aims to develop a direct synthetic approach for producing carbon materials from environmentally friendly biomass precursors at low cost. The key objectives of the study are outlined as follows:

1. To synthesize biocarbon materials from leaves of *Spathodea campanulata* and *Tecoma capensis* using direct pyrolysis technique

2. To synthesize nitrogen doped material from prepared biomass carbon material

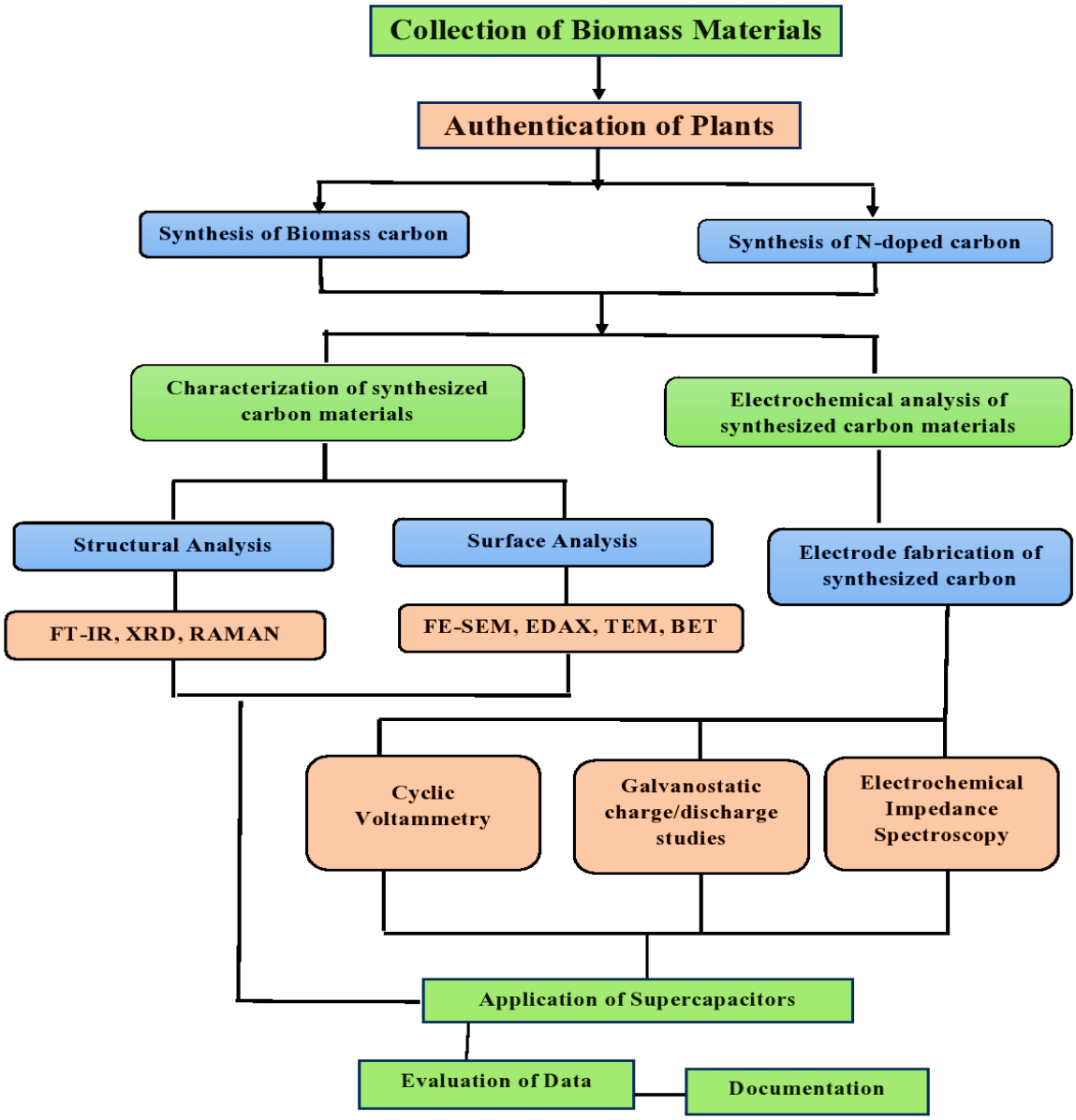
3. To characterize the synthesized biocarbon and doped biocarbon material by structural characterization (FT-IR, XRD, and Raman spectroscopy), morphological characterization (FESEM, HRTEM, and BET analysis)

4. To Derive Carbon Electrodes from the prepared carbon and to assess the electrochemical performance of the bio-carbon electrodes in supercapacitor using Electrochemical characterization through Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD), and Electrochemical Impedance Spectroscopy (EIS) for energy storage applications.

By pursuing these objectives, the research aims to advance the understanding and application of biomass-derived carbon materials for supercapacitor technology, offering a sustainable and cost-effective solution for energy storage needs.

Conceptual Framework

The adopted conceptual framework is depicted below



Methodology

The work plan for the present investigation is structured into three phases:

Phase I: Synthesis of carbon materials (SPL/TCL) and nitrogen doped carbon from *Spathodea campanulata* and *Tecoma capensis* (SN/TN) Leaves

Phase II: Physiochemical and Morphological characterization of synthesized carbon materials-SPL/TCL/SN/TN

Phase III: Electrochemical characterization of SPL/TCL/SN/TN derived carbon materials for utilization of synthesized carbon materials in supercapacitor electrode applications

By systematically carrying out these three phases, the research aims to gain insight into the synthesis, physicochemical properties, electrochemical behavior, and practical application of carbon materials derived from SPL and TCL leaves for supercapacitor technology.

Phase – I:

Direct pyrolysis of *Spathodea campanulata* leaves & *Tecoma capensis* leaves

10g of collected dry leaves of *Spathodea campanulata* and *Tecoma capensis* were subjected to direct pyrolysis in an alumina crucible in a tubular furnace under nitrogen atmosphere. The pyrolysis was conducted at temperatures of 700°C, 800°C, and 900°C for a duration of three hours. The resulting carbonized solid was subjected to washing with 5M HCl and dried at 60°C overnight. The carbonized materials obtained at different temperatures were designated as SPL-700, SPL-800, SPL-900, TCL-700, TCL-800, and TCL-900 respectively (Biswal *et al.*, 2013).

Synthesis of Nitrogen- doped carbon materials

The prepared carbon material (SPL-700, SPL-800, SPL-900, TCL-700, TCL-800, and TCL-900) was mixed with urea in the ratio of 3:1 (Urea: carbon) to facilitate nitrogen incorporation into the carbon materials. The mixture was thoroughly homogenized at ambient conditions with intermittent stirring over a period of 12 hours. The homogeneous mixture was transferred into a ceramic crucible, placed in a tubular furnace and subjected to three different activation temperatures: 700°C, 800°C, and 900°C, with a heating rate of 5°C/min, under an inert atmosphere for 2 hours to initiate the doping process in the carbon materials. Following doping, the resultant mixture was washed repeatedly with deionized water to remove any residual impurities and maintain a neutral pH. The washed samples were then dried in a hot

air oven at 60°C overnight to ensure complete drying. The doped materials were designated as SN-700, SN-800, SN-900, TN-700, TN-800, TN-900.

Phase – II: Physiochemical characterization of synthesized carbon material and doped material

The physicochemical characteristics of the synthesized carbon material and nitrogen doped carbon materials were analyzed using

- Fourier-transform infrared spectroscopy (FT-IR) (Perkin Elmer FT-IR spectrophotometer), for the examination of molecular vibrations and functional groups present in the carbon materials.
- X-ray diffraction (XRD) analysis [ULTIMA IV Model X-ray diffractometer equipped with CuKα radiation (λ = 1.5406 Å)] over a range of 10–90° with a count time of 0.2 seconds at 0.02° steps to ascertain the crystalline structure and phase composition of the carbon materials.
- Raman spectroscopy coupled with atomic force microscopy (AFM) imaging was carried out [WiTec alpha 300 confocal Raman microscope] for the characterization of molecular vibrations and structural properties of the carbon materials at a microscopic level.

Morphological characterization of synthesized carbon material and doped material

Surface morphological characteristics of the synthesized carbon materials were investigated using TESCAN MIRA3 XMU Field Emission Scanning Electron Microscope, Transmission Electron Microscopy (TEM) with a voltage of 120 kV (FEI Tecnai G2), and BET analysis using Quantachrome Instruments of ASiQwin (Version.3).

Phase – III: Electrochemical characterization of synthesized carbon material and doped material

To investigate the electrochemical properties of the synthesized functional carbon electrode materials, the prepared SPL/TCL/SN/TN as a carbon source, ketjen black as carbon conductive additive, and polyvinylidene fluoride (PVDF) as binder were combined in a weight ratio of 80:15:5 dissolved in N-methyl-2-pyrrolidone (NMP) solvent. Once the slurry was thoroughly dispersed, it was coated onto a graphene sheet with a surface area of 1 cm^2. The coated slurry was then dried in a hot vacuum oven at 100°C for 24 hours to evaporate the solvent.

1 M H_2SO_4 electrolyte was employed in a three-electrode system configuration. For this setup, the synthesized carbon electrode active materials derived from SPL/TCL/SN/TN were used as the working electrode, while a saturated calomel electrode (SCE) served as the reference electrode and platinum acted as the counter electrode. The electrochemical performance of the prepared functional carbon materials was evaluated through Cyclic Voltammetry (CV) and Galvanostatic Charge/Discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS) analyses using a CH Instrument, Model CHI608E, USA. Specific capacitance, energy density, and power density were calculated using established equations as per the references cited. (Byatarayappa *et al.*, 2021)

Results

The salient features pertaining to the present study entitled **"**Investigation of Biomass Derived Functional Carbon Electrodes from leaves of *Spathodea campanulata* and *Tecoma capensis* for Supercapacitor applications**"** are summarized below:

PHASE I

Carbon materials and doped carbon materials were synthesized using procedure detailed in methodology section and designated as SPL-700, SPL-800, SPL-900, TCL-700, TCL-800, TCL-900 SN-700, SN-800, SN-900, TN-700, TN-800, TN-900

PHASE II

By utilizing advanced analytical techniques, comprehensive insights into the physicochemical properties of the synthesized pyrolyzed and functionalized carbon materials were obtained, facilitating a detailed understanding of their structural characteristics and functional groups.

- XRD analysis of the carbon materials synthesized via direct pyrolysis technique indicate the amorphous nature of SPL-700, SPL- 800, SPL-900, SN-700, SN-800, SN-900, TN-700, and TN-800. In contrast, carbon materials such as TCL-700, TCL-800, TCL-900 and TN-800 exhibit a crystalline nature.
- FT-IR spectra of all synthesized carbon materials derived from both precursors indicate the presence of functional groups such as OH, C=O, and C-O on the surface.
- Raman spectroscopy analysis of the synthesized carbon materials confirmed the presence of characteristic D and G bands at approximately 1350 cm^{-1} and 1590 cm^{-1}, respectively. The observed I_D/I_G ratio below 1 indicate a low degree of graphitization in the prepared carbon materials

- Energy-dispersive X-ray spectroscopy (EDS) analysis confirmed the major elemental composition present in the synthesized carbon materials. The predominant presence of carbon and oxygen aligned with the findings of FT-IR studies.
- The microporous structure observed in the FESEM images of the synthesized carbon materials confirmed the development of micro and mesopores on the surface of the carbon materials.
- TEM images of SPL-900, TCL-900, SN-900, TN-900 samples clearly illustrate an interconnected porous spherical morphology. This morphology further corroborates the presence of pores within the carbon materials, indicating their potential for efficient ion transport and charge storage in electrochemical devices such as supercapacitors.
- BET adsorption-desorption isotherm studies highlighted the presence of micro and mesopore in the carbon materials.

PHASE III:

- The electrochemical capacitive behavior observed in the cyclic voltammetry (CV) profiles indicated significant electrical double-layer capacitance (EDLC) behavior along with low pseudocapacitive nature.
- Galvanostatic Charge/Discharge (GCD) measurements reveal a decrease in specific capacitance as the current density increased from 75μA/g to 250 μA/g. This decrease can be attributed to the rapid charging of the electrode. Conversely, lower current densities tend to yield higher specific capacitance, as micropores retain electrolyte ions without depletion.
- Among the examined carbon materials, maximum specific capacitance values were obtained at 338 F/g for SPL-900, 122 F/g for TCL-900, 450 F/g for SN-900, and 470 F/g for TN-900 .TN-900 exhibited good cyclic stability.
- Electrochemical Impedance Spectroscopy (EIS) analysis elucidate the physical and chemical processes occurring within the carbon materials. Low values of charge transfer resistance, coupled with semi-circle patterns observed in the high-frequency region, suggest a low ionic conductivity in the prepared carbon materials.
- The Ragone plot of SPL/TCL /TN and SN-derived carbon materials highlighted their potential in energy storage applications.
- Overall, these comprehensive analyses provide insights into the electrochemical behavior and surface morphology of the synthesized functional carbon electrode

materials, thereby contributing to the understanding of their suitability for energy storage applications.

Conclusion

Functionalized carbon materials, namely SPL- 700, SPL- 800, SPL- 900, TCL- 700, TCL-800, TCL- 900, SN- 700, SN- 800, SN- 900, TN- 700, TN- 800 and TN- 900 were successfully synthesized from dried *Spathodea campanulata* (SPL)and *Tecoma capensis* (TCL) leaves using direct pyrolysis techniques. Based on the results provided, it can be concluded that the prepared functional carbon electrode material (TN-900) exhibited superior ionic transport, high specific capacitance (Csp), increased energy (E) and power density (P) and good cyclic stability. This suggests that these materials possess favorable properties for applications in energy storage devices such as supercapacitors or batteries. Characterization of all synthesized carbon materials indicate that the selected precursors, *Spathodea campanulata* (SPL)and *Tecoma capensis* (TCL) leaves exhibit favorable properties for supercapacitor electrodes. Thus, it can be inferred that these selected precursors hold promise for imparting supercapacitive characteristics to the synthesized carbon electrode materials, making them suitable candidates for application in supercapacitors.

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